

The impact of phonon dispersion on thermodynamical properties in computational models of crystalline solids

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Abstract

The existing techniques of account for the phonon dispersion are computationally costly, while its impact on a variety of thermodynamic properties appears negligible. We develop a mathematical formalism, which allows for clear understanding of the effect. The theoretical elaborations are then confronted with a widely used phenomenological model of the dispersion relation. The results show that accuracy of the models, which neglect the phonon dispersion, allows for calculation of many thermodynamic quantities up to an admissible precision. Although the context refers mainly to the Helmholtz energy, other properties are concerned as well with less details. Time-efficient schemes of control over the accuracy loss due to the neglected phonon dispersion are discussed.

keywords: phonon dispersion, thermodynamic properties, Helmholtz energy

1 Introduction

The phonon dispersion represents a challenging problem in computational models of crystalline solids. As the analytical form of the dispersion relation is so far not established, the numerical techniques are inevitably come into use. The computational time demanded by these methods is by few orders longer than the one needed for calculation of the phonon frequencies solely at Γ -point. Despite the impressing power of modern computer resources, this is still quite costly calculation, e.g. in the quantum-mechanical treatment of problems.

On other hand, in practice it is often met, that some thermodynamic properties remain unaffected to the precision of interest by the phonon dispersion. That is, in such case the model restrained to consideration of

the crystal unit cell and its Γ -point frequencies would lead to a sufficient level of accuracy and decrease drastically the computational cost. Indeed in many theoretical studies the phonon dispersion is neglected for these reasons.

Nonetheless the question of reliability and validity of such approximation is sometimes doubted on fair scientific grounds, as seemingly there was given neither theoretical justification for this approach, neither clear theoretical notion on the impact of phonon dispersion on thermodynamic properties. In this work we present a purely theoretical study of phonon dispersion that lets conceive the problem on mathematical grounds and provide with altogether missing criteria to judge on its role in computational models. The elaborated mathematical treatment further will be applied to the existing phenomenological model widely used in both experimental and theoretical studies to give the understanding of why many thermodynamic properties appear insensitive to the phonon dispersion. Therefrom a theoretical justification for the discussed approximation follows.

All the reported work is performed with the Helmholtz energy expression as a sample thermodynamic quantity. However the mathematical statements will be kept as general as possible, thus the analogous treatment could be freely applied to other properties with minimal modifications. In Sec. 6 the concern on other thermodynamic properties and the boundaries of the approximation will be discussed.

2 Theoretical background

The concept of phonon dispersion arises from the cyclic periodic model of atomic lattice [1, 2]. That is, the whole lattice is represented as a pattern specified by a chosen crystal cell of p atoms, which is repeated N times by translation vectors. The commonly adopted harmonic model with Born-von Karman boundary condition leads to the description of nuclei motion in terms of $3p$ (3-dimensional case) normal modes and N allowed wave vectors. Together they form $3pN$ degrees of freedom. Further 6 normal modes (3 of translation and 3 of rotation) should be subtracted to yield the number of genuine vibrations [3]. For the model of infinite crystal, i.e. $N \rightarrow \infty$, the number of vibrational modes is $3p - 3$, as there are no rotations external to the infinite lattice. The dependence of the vibrational frequency ν_i of i -th normal mode on the wave vector κ , which varies over N values allowed by the boundary condition, is called the phonon dispersion relation. Its analytical form for a general 3-dimensional case is so far not established.

All allowed wave vectors can be found within the first Brillouin Zone (BZ), which is the reciprocal to the chosen cell of direct periodic lattice. The other vectors are symmetrically equivalent to those of the first BZ due to the periodicity of the dual lattice. When N tends to infinity, the uniformly spread wave vectors are treated as a 3-dimensional continuum.

According to the foundations of statistical physics the frequencies of vibratory motion can be used for evaluation of thermodynamic properties. As stated in the introduction, we'll consider specifically the expression

for Helmholtz energy $F = E_{st} + F_{vib} + E_{el}$ [4], where E_{st} , F_{vib} are the static lattice energy and the vibrational energy of nuclei, E_{el} is the term arising due to the presence of free electrons. In common practice these quantities are obtained per crystal cell (designated by the superscript cc): $F^{cc} = F/N = E_{st}/N + F_{vib}/N + E_{el}/N$. Similar forms of account for the vibrational motion occur in expressions for other thermodynamic potentials and properties, which will be briefly touched solely at the end of manuscript.

Regularly for insulating solids E_{el} is excepted from consideration. The only term, which concerns the frequencies of normal modes, is F_{vib} :

$$F_{vib} = F_{ZP} + F_{Th} = \frac{h}{2} \sum_{i=1}^{3pN} \nu_i + kT \sum_{i=1}^{3pN} \ln[1 - \exp(-\frac{h\nu_i}{kT})], \quad (1)$$

where F_{ZP} and F_{Th} are the zero-point and thermal constituents; h and k are the Planck and Boltzmann constants; T is the temperature. We remark, that the summation runs over all normal modes, including the translational ones, which have zero frequency. Obviously this does not affect the zero-point term. We do not amend the definition of the thermal part, which then stipulates taking the logarithm of 0, because it is not of importance when the problem will be brought into continuous case.

Taking into account the phonon dispersion relation the summation over frequencies can also be recast into the sum over the normal modes and the allowed wave vectors:

$$F_{vib} = \sum_{i=1}^{3p} \sum_{j=1}^N \left\{ \frac{h}{2} \nu_i(\boldsymbol{\kappa}_j) + kT \ln[1 - \exp(-\frac{h\nu_i(\boldsymbol{\kappa}_j)}{kT})] \right\}. \quad (2)$$

The frequencies of normal modes can be calculated in the least tedious manner at the zero wave vector [1, 2], also called Γ -point. Other points of BZ require more complicated schemes, which lead to procedures of drastically larger workload. The straightforward approach is to adopt a larger crystal cell. As it will contain more atoms, the increased number of normal modes corresponds merely to pieces of the same phonon dispersion branches in the smaller cell. However due to computational cost there exists a practice to include only the frequencies of normal modes at Γ -point in Eq. 2, thus attempting to approximate the vibrational part of Helmholtz energy expressed per crystal cell:

$$F_{vib}^{cc} \approx \sum_{i=1}^{3p} \left\{ \frac{h}{2} \nu_i(\boldsymbol{\Gamma}) + kT \ln[1 - \exp(-\frac{h\nu_i(\boldsymbol{\Gamma})}{kT})] \right\}. \quad (3)$$

The principle goal of this work is to study the theoretical significance of approximation given in Eq. 3. Particularly some emphasis will be given to its consequences in reconstruction of the dependence of Helmholtz energy on the cell volume (V^{cc}) in the analytical form $F^{cc}(V^{cc})$. It is obtained by means of curve fitting from the underlying dependence of E_{st} and ν_i on volume. This approach gained the name of quasi-harmonic model [4].

3 Developing mathematical formalism

The mathematical formalism developed in this section will be grounded on the existing treatment of the phonon dispersion in theoretical studies. Up to our knowledge there exist 2 distinct schemes. The first one (supercell approach) is perhaps the most straightforward. It follows directly from the underlying theory surveyed in Sec. 2. Another very popular model relies on the concept of phonon density of states. It was apparently inspired by experimental works where the signal intensities of measured vibrational frequencies lead to the natural treatment of problem in terms of density distribution.

We note that seemingly no mathematical formalization of the problem was reported to reveal the connection of these methods. In this section it will be developed for the case of Helmholtz energy. Thereon the equivalence of both approaches will be demonstrated.

3.1 Supercell approach

At first we discuss the supercell approach of accounting for the phonon dispersion, which is quite straightforward. Here the superscripts sc and uc will refer to the quantities calculated per supercell and unit cell respectively. The Helmholtz energy (F) of a supercell with dimensions $m_1 \times m_2 \times m_3$ according to Eq. 2 (without loss of generality in the following the term due to the free electrons is ignored for convenience as if be an insulator) is approximately:

$$F^{sc} = m_1 m_2 m_3 F^{uc} \approx m_1 m_2 m_3 E_{st}^{uc} + \sum_{i=1}^{3pm_1 m_2 m_3} \left\{ \frac{\hbar}{2} \nu_i^{sc} + kT \ln[1 - \exp(-\frac{\hbar \nu_i^{sc}}{kT})] \right\} = E_{st}^{sc} + \sum_{i=1}^{3pm_1 m_2 m_3} f_i^{sc}, \quad (4)$$

designating i -th mode calculated at the Γ point of the supercell by ν_i^{sc} , its vibrational contribution to the Helmholtz energy by f_i^{sc} and the static lattice energy of cell by E_{st} , whereas p is the number of atoms in the unit cell. The approximate equality becomes exact when $m_1 m_2 m_3 = N$ is the total number of the unit cells in the crystal. I.e. the phonon dispersion becomes completely accounted for. The supercell approach with $m_1 m_2 m_3 < N$ implies a certain approximate treatment of the phonon dispersion, which will be now explored.

Restarting from the full account of the phonon dispersion for the unit cell, we'll use the dependence of the energy $f_i^{uc}(\boldsymbol{\kappa}) = f(\nu_i^{uc}(\boldsymbol{\kappa}))$ on the wave vector $\boldsymbol{\kappa}$ that identifies a point in the reciprocal lattice. Onwards the superscript uc at f_i^{uc} and ν_i^{uc} will be dropped for brevity, because the respective functions of the supercell will not be involved further. A stack of Brillouin zones belonging to a supercell with dimensions $m_1 \times m_2 \times m_3$ divides the first Brillouin zone (BZ) of the unit cell in $m_1 m_2 m_3$ congruent volumetric elements. These elements contain an equal number of wave vectors allowed by Born-von Karman boundary condition $\Delta N = N/(m_1 m_2 m_3)$, as all vectors are uniformly spread according to the

translational symmetry of the reciprocal lattice. The Γ point frequencies of the supercell normal modes correspond to the frequencies of normal modes at $m_1 m_2 m_3$ distinct wave vectors of the unit cell first BZ.

For instance, when $m = m_1 = m_2 = m_3$, there are 8 meshes with $\nu_i(\boldsymbol{\kappa})$ known at 8 points $\boldsymbol{\kappa}_j$, $j = 1..8$ laying on the BZ border. Then the number of wave vectors ΔN per element $\Delta \boldsymbol{\kappa}$ (the volume of the supercell BZ) is $\frac{\Delta N}{\Delta \boldsymbol{\kappa}} = \frac{N}{m_1 m_2 m_3 \Delta \boldsymbol{\kappa}} = \frac{N}{8 \Delta \boldsymbol{\kappa}}$. With each mesh $\Delta \boldsymbol{\kappa}$ labeled by number j , one can associate the function value $f(\boldsymbol{\kappa}_j)$, as there's only one node which belongs to that mesh and at which the frequency $\nu_i(\boldsymbol{\kappa}_j)$ is known. Furthermore in the limit of a supercell $m \rightarrow \infty$ spanning the whole infinite crystal we have $\lim_{m \rightarrow \infty} \Delta \boldsymbol{\kappa} = 0$.

Considering f_i as a continuous function of $\boldsymbol{\kappa}$, a summation over wave vectors of the unit cell first BZ with volume V_{BZ}^{uc} can be approximated by a Riemann sum on an equidistant grid:

$$\begin{aligned} F_{vib}^{uc} = F_{vib}/N &= \frac{1}{N} \sum_{i=1}^{3p} \sum_{j=1}^N f_i(\boldsymbol{\kappa}_j) \approx \frac{1}{N} \sum_{i=1}^{3p} \sum_{j=1}^{m_1 m_2 m_3} f_i(\boldsymbol{\kappa}_j) \Delta N \\ &= \sum_{i=1}^{3p} \sum_{j=1}^{m_1 m_2 m_3} f_i(\boldsymbol{\kappa}_j) \frac{\Delta N}{N \Delta \boldsymbol{\kappa}} \Delta \boldsymbol{\kappa} \xrightarrow{\Delta \boldsymbol{\kappa} \rightarrow 0} \sum_{i=1}^{3p} \int_{V_{BZ}^{uc}} f_i(\boldsymbol{\kappa}) \frac{d \ln N}{d \boldsymbol{\kappa}} d \boldsymbol{\kappa}. \quad (5) \end{aligned}$$

The integral in Eq. 5 is the exact expression of F_{vib}^{uc} in the model of infinite crystal. The quantity written explicitly

$$\frac{d \ln N}{d \boldsymbol{\kappa}} = \frac{d N}{N d \boldsymbol{\kappa}} = \lim_{\substack{\Delta \boldsymbol{\kappa} \rightarrow 0 \\ m \rightarrow \infty}} \frac{m^{-3}}{\Delta \boldsymbol{\kappa}} = \lim_{\substack{\Delta \boldsymbol{\kappa} \rightarrow 0 \\ m \rightarrow \infty}} \frac{(V_{BZ}^{uc}/V_{BZ}^{sc})^{-1}}{V_{BZ}^{sc}} \equiv (V_{BZ}^{uc})^{-1} \quad (6)$$

is important to preserve the energy units of measure. So it leads to a simpler expression for infinite crystal with the direct lattice unit cell volume $V^{uc} = (V_{BZ}^{uc})^{-1}$:

$$F_{vib}^{uc} = V^{uc} \sum_{i=1}^{3p} \int_{V_{BZ}^{uc}} f_i(\boldsymbol{\kappa}) d \boldsymbol{\kappa}. \quad (7)$$

For the equidistant grid given by a supercell as discussed above, the Riemann sum of Eq 5 now can be reduced to:

$$\begin{aligned} F_{vib}^{uc} &\approx \frac{1}{N} \sum_{i=1}^{3p} \sum_{j=1}^{m_1 m_2 m_3} f_i(\boldsymbol{\kappa}_j) \frac{N}{m_1 m_2 m_3} \\ &= (m_1 m_2 m_3)^{-1} \sum_{i=1}^{3p} \sum_{j=1}^{m_1 m_2 m_3} f_i(\boldsymbol{\kappa}_j). \quad (8) \end{aligned}$$

Such estimation of the integral in Eq. 7 corresponds to a piecewise linear approximation of the phonon dispersion relation. In the case of $m = m_1 = m_2 = m_3 = 2$, it degrades to the simplest linear interpolation. For $m = 1$, the formula is reduced to the unit cell approach with $\Delta \boldsymbol{\kappa} = V_{BZ}^{uc}$ being the unit cell BZ itself, i.e. this leads to the expression that neglects the

phonon dispersion:

$$F_{vib}^{uc} \approx V^{uc} \sum_{i=1}^{3p} f_i(\mathbf{\Gamma}) V_{BZ}^{uc} = \sum_{i=1}^{3p} f_i(\mathbf{\Gamma}). \quad (9)$$

The phonon dispersion can be neglected, when the major part of the hyper-volume (the integration on BZ volume) under the hyper-surface $f_i(\mathbf{\kappa})$ is $f_i(\mathbf{\Gamma}) \times V_{BZ}^{uc}$, that corresponds to the integration of the flat "horizontal" hyper-surface defined by the function value $f_i(\mathbf{\Gamma})$. As practically the frequencies of optic modes do not change for various wave vectors the order of magnitude, it can be expected. Therewith the higher order terms become a small correction, i.e. the approximation implied is a truncation to a certain precision. This criteria purely relies on the "flatness" of the vibrational energy dependence on wave vector, particularly, the absence of soft modes is not required. Hence the role of the phonon dispersion is guided by the range of the vibrational energy contribution functions f on the BZ. However the acoustic branches routing at 0 Hz frequency of the translational modes at the Γ point still may undergo large variations of frequency. All this will be discussed properly in Sec. 4.

3.2 Phonon density of states approach

A different approach frequently met in theoretical studies involves the phonon density of states (DoS), which is equivalent to the described above under the following consideration. We'll normalize DoS $G(\nu) = 3p \frac{dN}{d\nu}$ of the whole crystal to obtain the frequency distribution function $g(\nu)$ [1]:

$$\frac{1}{3pN} \int_{-\infty}^{+\infty} G(\nu) d\nu = \int_{-\infty}^{+\infty} g(\nu) d\nu = 1. \quad (10)$$

The frequency distribution function can be expanded as a sum of the contributions from individual normal modes $g(\nu) = \sum_{i=1}^{3p} \rho_i(\nu)$. The mathematical flow can be fulfilled regarding the one-mode distributions ρ_i with the summation applied afterwards. We'll further expand the Riemann sum from Eq. 5 into a triple summation where the grid nodes are indexed along the coordinate axes of reciprocal lattice from $\mathbf{\kappa}_{111} = \mathbf{\Gamma}$ to $\mathbf{\kappa}_{m_1 m_2 m_3}$:

$$\begin{aligned} F_{vib}^{uc} &= \frac{1}{N} \sum_{j=1}^{m_1 m_2 m_3} f_i(\mathbf{\kappa}_j) \Delta N \\ &= \sum_{a=1}^{m_1} \sum_{b=1}^{m_2} \sum_{c=1}^{m_3} f(\nu_i(\mathbf{\kappa}_{abc})) \frac{\Delta N}{N} = \sum_{abc} f(\nu_{i,abc}) \frac{\Delta N}{N}. \end{aligned} \quad (11)$$

In the sum any 2 indices, e.g. b and c , select a row of meshes in the grid. Thus the double summation on these indices has a limit

$$\sum_{bc} = \sum_{b=1}^{m_2} \sum_{c=1}^{m_3} \xrightarrow{m_2, m_3 \rightarrow \infty} \int_{\inf \kappa_1}^{\sup \kappa_1} d\kappa_1 \int_{\inf \kappa_2}^{\sup \kappa_2} d\kappa_2 \quad (12)$$

(κ_1 and κ_2 are the coordinates in the reciprocal space), that can be viewed as a projecting operator that maps its operand defined on the 3-dimensional grid of meshes onto the 1-dimensional array labeled by the remaining third index a . Now we define

$$\Delta\nu_{i,abc} := \sup_{\kappa \in \Delta\kappa_{abc}} \nu_i(\kappa) - \inf_{\kappa \in \Delta\kappa_{abc}} \nu_i(\kappa) \quad (13)$$

and continue to expand the sum of Eq. 11:

$$\begin{aligned} F_{vib}^{uc} &= \sum_{abc} f(\nu_{i,abc}) \frac{\Delta N}{N} \\ &= \sum_{a=1}^{m_1} \sum_{bc} f(\nu_{i,abc}) \frac{\Delta N}{N \Delta\nu_{i,abc}} \Delta\nu_{i,abc} \xrightarrow{\Delta\kappa_{abc} \rightarrow 0} \int_{\inf \nu_i}^{\sup \nu_i} d\nu f(\nu) \rho_i(\nu). \end{aligned} \quad (14)$$

At last taking the summation over the contributions of all normal modes we arrive to the final expression:

$$\begin{aligned} F_{vib}^{uc} &= \sum_{i=1}^{3p} \int_{\inf \nu_i}^{\sup \nu_i} d\nu f(\nu) \rho_i(\nu) \\ &= \int_{\min_i \inf \nu_i}^{\max_i \sup \nu_i} d\nu f(\nu) \sum_{i=1}^{3p} \rho_i(\nu) = \int_{\min_i \inf \nu_i}^{\max_i \sup \nu_i} d\nu f(\nu) g(\nu). \end{aligned} \quad (15)$$

The problem of integration is then delegated to the estimation of the frequency distribution function $g(\nu)$. In practice it is obtained from the projection of all the vibrational frequencies together on the single Γ point. As demonstrated, it is an alternative solution of the integration problem as in the former approach (Sec. 3.1), because it is the same limit of the Riemann sum of Eq. 5. The mesh grid set up in both methods is used for the direct numerical evaluation of the integral at the former one, while in the latter it's employed for reconstruction of the intermediate function $g(\nu)$, which is then used as a weight function (normalized multiplicity) for the integral of $f(\nu)$.

When the linear interpolation is used to describe the phonon dispersion relation, which corresponds to the supercell approach of $2 \times 2 \times 2$ dimensions, the frequency distribution function is simply set to the uniform one:

$$\rho_i = u_i(\nu) = \begin{cases} 1/(\sup \nu_i - \inf \nu_i), & \text{if } \inf \nu_i \leq \nu \leq \sup \nu_i \\ 0, & \text{otherwise} \end{cases} \quad (16)$$

Finally, the expression, which neglects the phonon dispersion, corresponds to a sharp peak of the density at $\nu_i(\mathbf{\Gamma})$, which can be described by the Dirac delta function $\rho_i(\nu) = \delta(\nu - \nu_i(\mathbf{\Gamma}))$. Although it is physically inaccurate as the infinite discontinuities are not expected $0 \leq \rho_i(\nu) \leq g(\nu) < 1 < \delta(0)$, this approximation is still valid when the dispersion branch is “flat”:

$$f(\nu_i(\mathbf{\Gamma})) = \int d\nu \rho_i(\nu) f(\nu) = \int d\nu \delta(\nu - \nu_i(\mathbf{\Gamma})) f(\nu). \quad (17)$$

4 Phonon dispersion integrals

Here we'll inspect in details the integration expressions derived for the vibrational contribution of each normal mode given by Eq. 7, namely:

$$V^{uc} \int_{V_{BZ}^{uc}} d\boldsymbol{\kappa} f_i(\boldsymbol{\kappa}) = V^{uc} \int_{V_{BZ}^{uc}} d\boldsymbol{\kappa} f(\nu_i(\boldsymbol{\kappa})), \quad (18)$$

which will be referred to as the phonon dispersion integral of i -th vibrational normal mode from here onwards, or simply the phonon dispersion integral with the summation index dropped. Now we'll note that by virtue of the mean value theorem, as the function f_i can be regarded continuous in the closed 3-dimensional interval \bar{V}_{BZ}^{uc} and differentiable in the open interval V_{BZ}^{uc} :

$$\exists \bar{\boldsymbol{\kappa}} \in V_{BZ}^{uc} : V^{uc} \int_{V_{BZ}^{uc}} d\boldsymbol{\kappa} f_i(\boldsymbol{\kappa}) = (V_{BZ}^{uc})^{-1} \int_{V_{BZ}^{uc}} d\boldsymbol{\kappa} f_i(\boldsymbol{\kappa}) = f(\nu_i(\bar{\boldsymbol{\kappa}})). \quad (19)$$

Therefore another perspective to look at the solution of phonon dispersion integral is the estimation of a special frequency $\bar{\nu}_i = \nu_i(\bar{\boldsymbol{\kappa}})$. Its value is approximated by $\bar{\nu}_i \approx \nu_i(\boldsymbol{\Gamma})$, when the dispersion is neglected.

The energy contribution function of *frequency*, which is monotonically increasing, in its explicit form is:

$$f(\nu) = f_{ZP}(\nu) + f_{Th}(\nu) = \frac{h}{2}\nu + kT \ln[1 - \exp(-\frac{h\nu}{kT})]. \quad (20)$$

The zero-point energy function f_{ZP} is linear and doesn't require complicated treatment, while the thermal energy function f_{Th} is slowly changing at high frequencies, but it drops down to $-\infty$ when $\nu \rightarrow 0$ and thus poses a problem of improper integral in the respective part. The latter concerns particularly the acoustic modes, which branches of dispersion relation start from 0 Hz. In fact, when the phonon dispersion is neglected, their contribution is completely discarded.

A convenient preparation is the variable substitution $x = h\nu/kT$ so that

$$f(x) = kT \frac{x}{2} + kT \ln[1 - \exp(-x)] = kT \{ \ln[\exp(x/2)] + \ln[1 - \exp(-x)] \} \\ kT \ln[\exp(x/2) - \exp(-x/2)] = kT \ln[2 \sinh(x/2)], \quad (21)$$

therewith accumulating the integrand terms in one. Let's denote the passing band of i -th normal mode by $I_i = [a_i, b_i]$ with $a_i = \inf \nu_i(\boldsymbol{\kappa})$ and $b_i = \sup \nu_i(\boldsymbol{\kappa})$. The error $\epsilon_f = |f_i(\bar{\boldsymbol{\kappa}}) - f_i(\boldsymbol{\Gamma})| < f(b_i) - f(a_i)$ tends to zero when the measure of passing band interval $\mu(I_i) < \delta_\nu$ is sufficiently small.

Before proceeding further we'll benefit from some practical considerations. The atomic vibrational frequencies are commonly found to lay within the Tera-Hertz order and less, rarely going up to the order of 100 THz. Thus we will fix the upper bound of frequency variations by one Peta-Hertz, which is seemingly quite an exaggerated value already. The optic modes, as empirically known, give a non-zero lower bound of the

interval ($a_i > 0$ Hz), which is greater by its absolute magnitude than the upper bound of the acoustic modes. Therefore we'll set the lower bound of a generic optic mode to 10^{-3} THz. The ensemble of optic modes usually cause a concentration of the total frequency distribution function roughly in vicinity of ~ 1 THz.

Along with the discussed empirical observations, to estimate the generic bounds of accuracy, when the phonon dispersion is neglected, we'll employ a widely used successful model for the dispersion relation of vibrational modes proposed by Kieffer [5].

4.1 Acoustic modes

The acoustic modes as was explicated earlier pose a problem of improper integration. The corresponding value of phonon dispersion integral (Eq. 18) essentially depends on the rate with which the frequency approaches zero. At high frequency range the energy contribution function f_{ac} is usually as flat as of an optic mode. When the phonon dispersion is neglected and the acoustic branches are discarded from the calculations, these terms together can be considered as an additive constant: this is not of importance for energy quantities (which are usually determined up to an arbitrary constant). The role of this contribution might be observed solely when a thermodynamic potential is differentiated, if the value of the phonon dispersion integral is appreciably changing with the respective variable. Therewith the approach is suitable under the condition:

$$\left| \frac{\partial f_{ac}(\bar{\kappa}(V^{uc}))}{\partial V} \right| \leq \epsilon_{ac}, \quad (22)$$

which puts the limits on the accuracy of approach. According to Kieffer's model, the frequency distribution function of an acoustic mode takes a general form:

$$\rho_{ac}(\nu) = \frac{(2/\pi)^3 \arcsin(\nu/b_{ac})}{p(b_{ac}^2 - \nu^2)^{1/2}}, \quad (23)$$

where $\int_{I_{ac}} d\nu \rho_{ac}(\nu) = (3p)^{-1}$, p is the number of atoms in the unit cell and b_{ac} is the top frequency of the passing band, which is the only parameter allowing for variation of the modeling expression. In Table 6 the values of the phonon dispersion integral for acoustic modes obeying Kieffer's model are given for various parameters b_{ac} and temperatures.

Once the contribution of acoustic branches is considered as a constant, perhaps the maximum uncertainty imposed on the vibrational part of Helmholtz energy is $0.37 \text{ Ha} \cdot 3p^{-1}$ for the variation of upper bound frequency $\sim 10^{15}$ Hz, as seen from Table 6. It leads to the conclusion that the derivative with respect to frequency is remarkably small. Admitting such large variation in response to stretching/compression of the volume is clearly an impractically excessive exaggeration, whereas the factor $3p^{-1}$ might reduce the discarded contribution by few orders of magnitude. Indeed such accuracy is superfluous in many kinds of calculations. For instance, the static lattice energy usually has order of KHa and ensures high precision with respect to the neglected contribution.

4.2 Optic modes

Kieffer's model suggests to describe the whole ensemble of optic branches by the uniform distribution contributing to the total frequency distribution function (optic continuum [5]), except for few well identified normal modes. For the latter the Dirac δ -function is proposed to model their frequency distribution with generally sufficient accuracy. It can be confronted directly with Eq 17 to confirm that their dispersion relation leads to a flat function f_i , as the dispersion relation itself is flat. Subtracting the number of such optic modes q from the total, there are $3p - 3 - q$ modes participating in the optic continuum.

Let's denote the interval of optic continuum as a passing band I_{op} . Usually the dispersion branches are restricted from crossing each other at the same point κ due to the symmetry considerations. Therefore they are commonly arranged in a stack and bound each other from above and below. This allows for a rough estimation of the passing band of each optic mode in the continuum $I_i \approx [a_i, a_i + \mu(I_{op})/(3p - 3 - q)]$. Therewith a pragmatic approximation of the error due to the negligence of phonon dispersion in i -th mode might be:

$$\begin{aligned} \epsilon_i &= |f_i(\bar{\kappa}) - f_i(\Gamma)| \approx \left| \frac{df(\nu_i(\Gamma))}{d\nu_i} (\nu_i(\bar{\kappa}) - \nu_i(\Gamma)) \right| \\ &\approx \left| \frac{df(\nu_i(\Gamma))}{d\nu_i} \right| \frac{1}{2} \mu(I_i) \approx \left| \frac{df(\nu_i(\Gamma))}{d\nu_i} \right| \frac{\mu(I_{op})}{2(3p - 3 - q)}, \quad (24) \end{aligned}$$

which follows from the linear approximation of the dispersion relation. From simple calculus one can find $|\frac{df(\nu)}{d\nu}| < 10^{-12}$ on the domain $[10^{-3}, 10^3]$ THz, while the relation $|\frac{df(\nu)}{f(\nu)d\nu}|$ is $\sim 10^{-10}$ and $\sim 10^{-11}$ at 10^{-3} and 10^3 THz, respectively. On multiplication by $\frac{\mu(I_{op})}{2(3p-3-q)}$ this ensures a certain precision for the Helmholtz energy, when the phonon dispersion is not taken into account. Such precision is often admissible, if not superior to the sought one, for a variety of problems addressed in modern computational studies. For example, in the expression of Helmholtz energy the expected magnitude of errors in individual constituents of the vibrational term is strongly subdued by the static lattice energy, which usually has order of KHa.

5 Practical schemes

The general considerations presented in Sec. 4 reason the often discovered fact, that the phonon dispersion produces negligible effects on the Helmholtz energy. When the available computational resources are insufficient to take accurate account for the phonon dispersion, it may also justify the presumption that the modeled solid does not have peculiar features of the dispersion relations, which would produce significant deviation of the calculated quantities. Should the problem be still of concern and require a control, to spare computational time one can address the problem with the linear model of phonon dispersion, employing the calculations with $2 \times 2 \times 2$ supercell, because it efficiently gives the bounds

of phonon dispersion branches: larger cells will improve the accuracy less and less notably. If the aim of calculations relies on multiple evaluations for various parameters of the system, a scheme can be devised to spare the computational cost as follows.

As example we'll consider the reconstruction of Helmholtz energy dependence on crystal cell volume in analytical form at constant temperature by curve fitting procedure. This requires evaluation of $F^{cc}(V^{cc})$ for a set of volumes $\{V_i^{cc}\}$. One can perform the calculation for the unit cell while neglecting the phonon dispersion to find the array of points $\{(V^{uc}, F^{uc}(V^{uc}))_i\}$. Thereafter the phonon dispersion can be taken into account for a subset of values $\{V_j^{uc}\} \subset \{V_i^{uc}\}$ using a supercell to get $\{(V^{uc}, (m_1 m_2 m_3)^{-1} F^{sc}(m_1 m_2 m_3 V^{uc}))_j\}$. Then the error due to the phonon dispersion is estimated as:

$$\delta F^{uc}(V_i^{uc}) = (m_1 m_2 m_3)^{-1} F^{sc}(m_1 m_2 m_3 V_i^{uc}) - F^{uc}(V_i^{uc}). \quad (25)$$

This error can be then interpolated: i) complicated curve fitting procedures are unlikely to be much of use, given that there are few points $\{V_j^{uc}\}$; ii) it is important that the points $\{V_j^{uc}\}$ cover the whole studied domain of volume, i.e. $\min_i \{V_i^{uc}\} \in \{V_j^{uc}\}$ and $\max_i \{V_i^{uc}\} \in \{V_j^{uc}\}$. Besides that the interpolated error $\delta F(V)$ can provide with estimations at any point on the domain of volume, it allows for control over the accuracy of inferred thermodynamic quantities, such as pressure $P = -\partial F / \partial V$, the isothermal bulk modulus $K_0 = -V \frac{\partial P}{\partial V}$ and others, as will be explicated further.

If the interpolated error is considered as a finite variation of Helmholtz energy function of volume, simple formulae for the variation of derived quantities follow:

$$\delta P[F(V)] = P[F(V) + \delta F(V)] - P[\delta F(V)] = -\frac{\partial \delta F(V)}{\partial V} \quad (26)$$

$$\delta K[F(V)] = V \frac{\partial^2 \delta F(V)}{\partial V^2} \quad (27)$$

Alternatively, the interpolated error can be used as a correction function: the values, which should be used in fitting of Helmholtz energy vs. volume curve, would be $\{(V^{uc}, F^{uc}(V^{uc}) + \delta F(V^{uc}))_i\}$. Thus the effect can be directly observed in numbers. The advantage of the former approach is that the effect can be tackled analytically by means of calculus.

6 Discussion

Although the theoretical considerations were presented for the Helmholtz energy, completely analogous ideas are applicable also to some other thermodynamic properties (e.g. internal energy, entropy), as the terms affected by the phonon dispersion enter the respective expressions in a similar mathematical form [4]. Certainly the negligible sensitivity of these quantities to the phonon dispersion is connected with the peculiarities of their mathematical definitions.

Another important aspect is the overwhelming role of static lattice energy (due to its magnitude) in such properties as internal energy, bulk

modulus and others. As the consequence, the computational models are robust against uncertainties in the description of lattice dynamics up to a good precision, which is characterized by the relative error in calculations. Other properties, e.g. the thermal expansion of solids, which is very small quantity compared to compressibility, require more accurate techniques. Therefore its determination is quite challenging task (not only for computational methods, but also for measurements).

The effect of phonon dispersion may be rather more important to the quantities, which require theoretical models of high accuracy, like thermal expansion or Gruneisen parameter. Perhaps, one of the reason is that they are more closely related to the microscopic properties and description of the system. Besides, both thermal expansion and Gruneisen parameter are well known to be affected by the anharmonicity of vibrations (moreover the anharmonicity plays a crucial role in the phenomenon of thermal expansivity). In its turn, the anharmonicity is an important factor that determines the phonon density of states along with the phonon dispersion. And thus it raises altogether a question on the interaction of both concepts and the level of approximation achieved when one of the two is neglected.

In our opinion the materials exposed in this manuscript provide with convincing arguments which lead to conclusions: i) the inclusion of phonon dispersion into the computational model allows for systematic improvement of accuracy; ii) the negligence of phonon dispersion does not deprives the model of the validity in presence of other theoretical assumptions, moreover the loss of accuracy can be expected to be negligible for many problems of concern.

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Table 1: Phonon dispersion integral of acoustic modes obeying Kieffer's model for various parameters and temperatures.

Parameter b_{ac} , Hz	Phonon dispersion integral, $\text{Ha} \cdot (3p)^{-1}$	
	300 K	3000 K
10^{15}	0.0671	0.0671
10^{13}	0.0004	-0.0188
$5 \cdot 10^{12}$	-0.0003	-0.0254
$3 \cdot 10^{12}$	-0.0008	-0.0302
10^{12}	-0.0019	-0.0406
10^{11}	-0.0041	-0.0625
10^{10}	-0.0062	-0.0844
10^9	-0.0084	-0.1063
1	-0.0281	-0.3032